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IN A FUEL CELL FUNCTIONING AT HIGH TEMPERATURE

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Use of a Mixture of Molten Halides as the Electrolyte in a Fuel Cell Functioning at High Temperature

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The plotting of current — voltage curves in a medium of molten chlorides has made possible the study of the electrochemical behavior of several oxidants and fuels. This study was conducted as a part of a program to develop a fuel cell functioning at a high temperature and using a mixture of halides as electrolyte.

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Fuel cells functioning at a high temperature most frequently use an electrolyte consisting of a mixture of molten alkali carbonates, which may or may not be impregnated in a refractory porous matrix [1]. Recent studies on molten halide media and, in particular, on the eutectic LiCl-KCl [2, 3], have demonstrated electrochemical properties of these materials that make it possible to envisage their use as the electrolyte in fuel cells.

The operational characteristics of a fuel cell may be deduced from the current — voltage curves of the fuel and of the oxidant used in the electrolyte. We have studied qualitatively the electrochemical behavior of the oxidants and fuels under consideration by determining their current voltage curves in a medium of molten halides. At the temperatures under consideration, the majority of these oxidants and fuels are gaseous and insoluble in the electrolyte. Since current — voltage curves cannot be plotted using the conventional immersed electrode, we worked with a partially immersed electrode, according to a technique previously used in aqueous media [4].

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The electrolyte used was a eutectic mixture of LiCl and KCl, fused without special precautions in an inert atmosphere in order to eliminate moisture [2]. The introduction of a known amount of potassium hydroxide fixed the

p (O⁼) of the bath at 2.5. The indicator electrode was a thin plate of gold in the form of an equilateral triangle, each side 1 cm in length, suspended at the apex. The counter-electrode, consisting of a Pyrex tube containing several milliliters of fused eutectic in which a gold wire was immersed, had a resistance of the order of $1,000 \Omega$. The reference electrode consisted of a platinum wire immersed in a Pyrex tube containing a eutectic mixture with a known concentration of Pt^{++} ions.

With the aid of a potentiostat, the voltage of the indicator electrode was changed discontinuously in steps of 50 mV. The current was read under steady state conditions 2 minutes after the voltage was adjusted. The current — voltage curves were plotted for electrolyte temperatures in the $500°C$ range. The region, in which the electrolyte is electrically active extends, under these conditions, from -1.4 V (which corresponds to the reduction of OH^-) to approximately O V.

The polarographic curves of reduction of pure oxygen and of air were plotted at one atmosphere of these gases. They give the same type of curve, similar to those of the waves obtained during the reduction of compounds in solution.
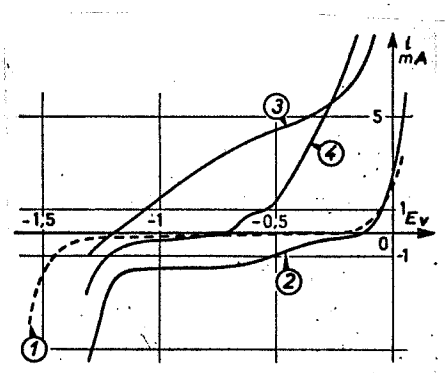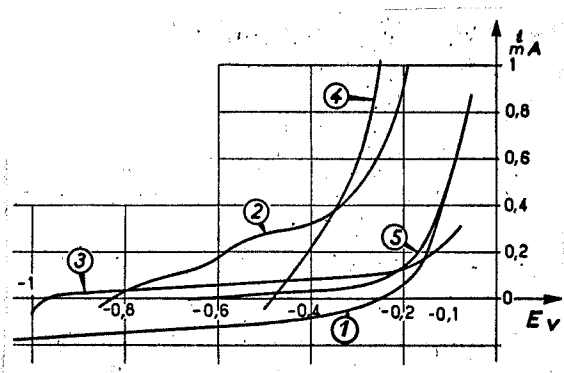

Fig. 1.

Fig. 1. Reduction of oxygen and oxidation of hydrogen and of carbon. Current — voltage curves: (1) the electrolytic carrier in an inert atmosphere, (2) reduction of oxygen (1 atm), (3) oxidation of hydrogen (1 atm), (4) oxidation of the indicator carbon electrode.

Fig. 2. Oxidation of carbonaceous fuels. Current — voltage curves: (1) the electrolytic carrier alone, (2) CO (1 atm), (3) vapors of petroleum ether entrained by an inert gas, (4) butane (1 atm), (5) hexane vapors entrained by an inert gas.
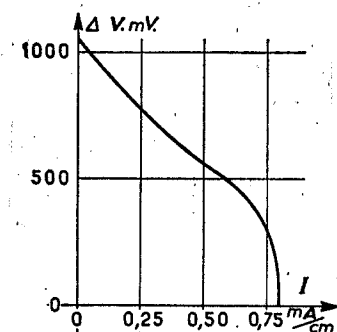
Fig. 3. Charge characteristics of an elementary hydrogen-oxygen cell in a medium of molten LiCl-KCl at 500°C. V, voltage at the boundaries; I, current per linear centimeter of three-phase contact.

The current corresponding to the plateau is reproducible only with difficulty; the plateau observed for oxygen has a height approximately double that obtained for air. In both cases, the process of reduction at the electrode appears to occur as a reaction at the triple line at the contact of the three phases: gaseous fuel, solid electrode, and liquid electrolyte; we determined, in fact, by changing the depth to which the electrode was immersed in the molten bath, that the current increased with the length of the three-phase line, and not with the amount of electrode surface immersed in the electrolyte. The potential at zero current is identical for air and oxygen, and is close to -0.15 V.

Hydrogen, carbon monoxide, a petroleum ether fraction, industrial butane, hexane, and carbon were studied as fuels. The curves for H_2, CO, and C_4H_{10} at one atmosphere of these gases were plotted. The hexane and the petroleum ether were carried off in the form of vapor by bubbling an inert gas through the slightly heated liquid. A graphite bar 5 mm in diameter was substituted for the gold indicator electrode for the study of carbon.

The curves that were obtained are shown in Figs. 1 and 2. It was found that the zero current potentials obtained for carbon, butane, and hexane are not in agreement with the data corresponding to the thermodynamic equilibrium of combustion, while that of oxygen is; a kinetically slow reaction must therefore intervene. On the other hand, the difference in zero current potential that is given by the curves for H_2 and CO, is nearly equal to that predicted on the basis of thermodynamic calculations. The oxidation currents are weak, except in the case of hydrogen; it is possible to increase them by raising the temperature of the molten bath.

The superposition of the current — voltage curves for hydrogen and for oxygen show that a hydrogen-oxygen cell, under the conditions under which these curves were plotted, possesses the charge characteristics shown in Fig. 3.

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